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INTERACTIONS OF MOLECULAR AND ION BEAMS WITH SURFACES.(U)
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Low kinetic energy active ion bombardment of transition metals, Si, Ge, Sn, Pb, graphite, and diamond have shown that chemical reactions can be induced between ion beams and surfaces. These reactions are specific and selective with respect to the ion-target combination and the thickness of the reacted layer can be controlled by varying the ion energy. The techniques of x-ray and UV photoelectron spectroscopy, Auger spectroscopy, secondary ion mass spectrometry (SIMS) and thermal desorption spectrometry (TDS) under ultra-high vacuum conditions are used to characterize the products of the beam-surface reactions. The reaction of		

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20. 30-3000 eV nitrogen beams with the first-row transition metals results in the formation of metal nitrides. The amount of nitrogen reacting with the metal can be correlated to the enthalpy of formation of the metal nitride. Reactions of nitrogen with M, MO, and MO_2 (M = Si, Ge, Sn, Pb) produces nitrides with no evidence for nitrate, nitrite, or nitroso formation in the oxides. A mechanism is proposed for the reaction which involves charge exchange neutralization and dissociation of the ion at the surface followed by penetration into the lattice, thermalization, and finally chemical reaction. SIMS experiments have shown that large molecular clusters, e.g., $H(H_2O)_5^+$, $Cs_4V_3^+$, W_3^+ , can be sputtered by collisions of single primary ions.

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MOLECULAR ORBITAL STUDY OF THE CHEMISORPTION OF
CARBON MONOXIDE ON A TUNGSTEN (100) SURFACE

by

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ABSTRACT

The adsorption energies of carbon monoxide chemisorbed at various sites on a tungsten (100) surface have been calculated by extended Huckel molecular orbital theory (EHMO). The concept of a "surface molecule" in which CO is bonded to an array of tungsten atoms W_n has been employed. Dissociative adsorption in which C occupies a four-fold, five-coordination site and O occupies either a four- or two-fold site has been found to be the most stable form for CO on a W surface. Stable one-fold and two-fold sites of molecularly adsorbed CO have also been found in which the CO group is normal to the surface plane and the C atom is nearest the surface. Adsorption energies and molecular orbitals for the stable molecularly and dissociatively adsorbed CO sites are compared with the experimental data on various types of adsorbed CO, i.e., virgin-, α -, and β -CO. Models are suggested for each of these adsorption types. The strongest bonding interactions occur between the CO 5σ orbital and the totally symmetric 5d and 6s orbitals of the W_n cluster. Possible mechanisms for conversion of molecularly adsorbed CO to dissociatively adsorbed CO are proposed and the corresponding activation energies are estimated.

ELECTROCHROMISM IN SOME THIN-FILM TRANSITION-METAL OXIDES
CHARACTERIZED BY X-RAY ELECTRON SPECTROSCOPY

by

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ABSTRACT

Qualitative results of an x-ray photoelectron and optical investigation of three thin-film transition-metal oxides, namely, WO_3 , MoO_3 , and V_2O_5 are reported. Data were obtained on films that were not colored and colored by an electrochromic process. The particular electrochromic coloration process used is electrolytic in nature and employs a sandwich-structure electrochromic cell and electrolyte pool. The optical spectra show increased absorption in the visible (red) and near-infrared spectral regions upon coloration. The photoelectron spectra for colored films exhibit a small band near the Fermi level and asymmetric band shapes for metal core-level bands which are absent in films that are not colored. The new band and the asymmetric band shapes are attributed to the presence of a reduced-state species caused by the presence of trapped electrons and metal bronze formation. Results from coloration with different electrolyte pools, i.e., H^+ , Li^+ , Na^+ , K^+ , Cs^+ , and Mg^{2+} electrolytes, are reported.

PHOTOCHROMISM AND ELECTROCHROMISM IN
AMORPHOUS TRANSITION METAL OXIDE FILMS

by

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ABSTRACT

XPS results for UV and electrolytically colored films of tungsten, molybdenum, and vanadium oxides show that upon coloration (1) reduced-state species of some of the metal ions are formed, (2) population of empty metal d bands located near the Fermi level results, and (3) charge-compensating ions cause bronze formation. Bleaching of the films causes a reversal of the processes. Due to the almost instantaneous coloration/bleaching possibilities, the films have considerable application as digital display devices.

MOLECULAR REARRANGEMENT AND CLUSTER FORMATION
IN SECONDARY ION MASS SPECTRA (SIMS) OF FLUORIDE SALTS

by

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ABSTRACT

Secondary ion clusters with mass greater than 700 amu, e.g., $K(KF)_{12}^+$, and up to 27 atoms, e.g., $Na(NaF)_{13}^+$, have been observed in the statis SIMS spectra of MF (M = Li, Na, K), $NaBF_4$, and KPF_6 . The long series of detected cluster ions of the type $M(MF)_n^+$ indicates that there is a high degree of stability associated with these clusters. The observation of such clusters in the $NaBF_4$ and KPF_6 spectra suggest that there is significant molecular rearrangement occurring in the secondary ion emission process from such salts. The secondary ion intensities provide a crude fit to the Saha-Eggert equation, yielding an electron temperature of $\sim 12,000$ K. The data are consistent with the plasma model of surface ionization in which arrangement and cluster formation occur in the plasma.

INTERACTIONS OF ION BEAMS WITH SURFACES. REACTIONS OF
NITROGEN WITH SILICON AND ITS OXIDES

by

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ABSTRACT

Ion beam studies of chemical reactions between nitrogen and surfaces of silicon and its oxides are reported. A spectrometer system designed for these studies which combines the techniques of x-ray and UV photoelectron spectroscopy, Auger electron spectroscopy, secondary ion mass spectroscopy, low energy electron diffraction, and ion bombardment is described. This work employs XPS and UPS to examine the products induced by 500 eV N_2^+ beams on targets of elemental Si, SiO, and SiO₂. The N_2^+ ions undergo charge exchange and dissociation at the surface of the target to form hot N atoms. Reaction with Si produces nitrides which are similar to those of the type Si₃N₄. Reaction with SiO and SiO₂ forms nitrides, with no evidence of nitrate or nitrite formation. The chemical nature of the reaction is suggested by identification of the reaction products through XPS and UPS and energy level shifts. The thickness of the silicon nitride layer on Si(111) formed by 500 eV N_2^+ bombardment has been determined to be ~19 Å thick by using the film/bulk Si XPS intensity ratio. Estimates obtained by depth-concentration profiling with 1 keV Ar⁺ and by using LSS projected ion range calculations agree with this approximate thickness.

X-RAY PHOTOELECTRON SPECTRA AND ELECTRONIC STRUCTURE
OF SOME DIAMINE COMPOUNDS

by

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ABSTRACT

The x-ray photoelectron spectra of some diamine molecules, namely urea, thiourea, guanidine hydrochloride, nitroguanidine, and cyanoguanidine have been measured. The data are consistent with an ionic structure for guanidine hydrochloride in which three nitrogen atoms of the guanidinium ion are chemically equivalent. The spectra also show that the N 1s levels of the three nitrogen atoms of the $\text{-NC(NH}_2\text{)}_2$ group in nitroguanidine and cyanoguanidine are essentially degenerate, indicating that these nitrogen atoms have similar atomic charges.

BODY OF REPORT

This report will briefly describe the advances made in instrumentation and will summarize the scientific work accomplished by providing the abstract of each paper published under Army support.

Instrumentation:

Our spectrometer facilities are housed in three UHV chambers. System I has capabilities of x-ray and UV photoelectron spectroscopy, Auger spectroscopy, and thermal desorption spectrometry. System II is used for secondary ion mass spectrometry. System III has all the capabilities of System I with the addition of reaction chamber in which reactions can be carried out under high temperature and high pressure conditions. The reacted sample will be introduced directly into the UHV system for spectroscopic analysis. This capability is just being completed and will greatly facilitate our studies of adsorption, desorption, and decomposition kinetics and their relationship to flaking in gun barrels. The ion beam accelerator is nearing completion; this will provide the capability of low-energy active ions in the UHV system. This will provide some of the most definitive results on transfer of ion kinetic energy into chemical reaction energy because of its low-energy capability and the array of other surface analysis equipment associated with it.

Scientific Work:

(See original reports)

B I B L I O G R A P H Y

- a.** "XPS and UPS Study of the Valence Band Structure and Chemisorption of Ti(0001)," Surface Sci., submitted.
- b.* "Clustering Distances Critical to Metal Dimer Formation in the Secondary Ion Mass Spectra (SIMS) of Cesium Halides," J. Chem. Phys., 70, 4834 (1979).
- c.* "Chemical Reactions of N_2^+ Ion Beams with First-Row Transition Metals," J. Phys. Chem., 83, 209-212 (1979).
- d.* "Secondary Ion Mass Spectrometry of Molecular Solids: Cluster Formation During Ion Bombardment of H_2O , C_6H_6 , and C_6H_{12} ," J. Amer. Chem. Soc., 101, 1951-1958, ²(1979).
- e.* "Macromolecular Ionic Clusters of Water Detected by SIMS," Int. J. Mass Spectrom. Ion Phys., 29, 199-202, (1979).
- f.# "SIMS Study of the Mechanism of Cluster Formation During Ion Bombardment of Alkali Halides," J. Chem. Phys., 69, 4931-4938 (1978).
- g.# "Chemisorption of CO on (10 $\bar{1}$ 1) Titanium Studied by XPS, UPS, FDMS, and AIB," J. Chem. Phys., 69, 3452-3477 (1978).
- h.* "AIB Induced Chemical Reactions at Surfaces Detected by SIMS," Chem. Phys. Lett., 59, 346-358 (1978).
- i.* "Phase Transformation (hcp \rightarrow bcc) on a (10 $\bar{1}$ 1) Titanium Surface Studied by He II UPS," Phys. Rev., 18, 6191-6194 (1978).
- j.# "Surface Alteration of Graphite, Graphite Monofluoride, and Teflon by Interaction with Ar^+ and Xe^+ ," Appl. Surface Sci., 1, 503-514 (1978).
- k.# "Vacuum Ultraviolet Resonance Line Radiation Source from Rare Gas Atoms and Ions for UHV Photoelectron Spectroscopy," J. Electron Spectrosc., 14, 143-153 (1978).
- l.# "High Mass Secondary Ion Clusters of Caesium Iodide Detected by SIMS," Surface Sci., 76, L613-L617 (1978).
- m.# "Interactions of N_2^+ and NO^+ Ions with Surfaces of Graphite, Diamond, Teflon, and Graphite Monofluoride," J. Amer. Chem. Soc., 100, 4441-4447 (1978).

- n.# "Chemical Reactions of N_2^+ Ion Beams with Group IV Elements and Their Oxides," J. Electron Spectrosc., 13, 435-444 (1978).
- o.# "Molecular Orbital Study of the Adsorption of Carbon Monoxide on a Tungsten (100) Surface," Surface Sci., 75, 29-45 (1978).
- p.# "Electrochromism in Some Thin-Film Transition-Metal Oxides," J. Appl. Phys., 49, 409 (1978).
- q.# "Photochromism and Electrochromism in Amorphous Transition Metal Oxide Films," Accts. Chem. Res., 11, 170 (1978).
- r.# "Molecular Rearrangement and Cluster Formation in the Secondary Ion Mass Spectra (SIMS) of Fluoride Salts," Surface Sci., 74, 229 (1978).
- s.# "Interactions of Ion Beams With Surfaces. Reactions of Nitrogen With Silicon and Its Oxides," J. Chem. Phys., 68, 1776 (1978).
- t.# "X-Ray Photoelectron Spectra and Electronic Structure of Some Diamine Compounds," J. Electron Spectrosc., 11, 123 (1977).

*Reprints being sent under separate cover.

**Preprints being sent under separate cover.

#Reprints already sent in progress reports.

XPS AND UPS STUDY OF THE VALENCE BAND STRUCTURE AND CHEMISORPTION
OF TI(0001)

by

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ABSTRACT

Photoemission studies of the clean (0001) face of a titanium single crystal using UV and X-ray photoelectron spectroscopy (UPS and XPS) have revealed two maxima in the valence band density of states at ~ 0.5 and ~ 1.4 eV below the Fermi level. The 1.4 eV peak exhibits the following unusual characteristics: (i) its photoionization cross section decreases rapidly as incident photon energy increases, (ii) its UPS intensity is rapidly quenched by exposure to small doses of CO and N₂ but large doses of O₂ are required for the same effect, (iii) its UPS intensity decreases rapidly upon heating from $\sim 120^\circ\text{C}$ to $\sim 240^\circ\text{C}$. The 0.5 eV peak does not exhibit this behavior. The characteristics of the 1.4 eV peak along with the inability of the Debye-Waller factor to adequately fit the temperature dependence suggests that it is due to photoemission from an electronic structure that is either localized at the surface or whose angular resolved characteristics change upon chemisorption.

CLUSTERING DISTANCE CRITICAL TO METAL DIMER
FORMATION IN THE SECONDARY ION MASS SPECTRA (SIMS) OF CESIUM FLUORIDE

by

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ABSTRACT

Cs_2^+ has been measured in SIMS of KCl-CsCl solid solutions which $[\text{Cs}]/[\text{K}]$ varies from 10^{-1} to 10^{-5} . The data indicate that there is a maximum clustering distance, i.e., Cs-Cs distance, above which Cs_2^+ is not formed. This distance is $\sim 200 \text{ \AA}$ and $\sim 400 \text{ \AA}$ for He^+ and Ar^+ primary ions, respectively, and is independent of primary energy over the range 0.2 to 3.0 keV. The results are consistent with a mechanism in which bound secondary clusters consisting of atoms from contiguous as well as noncontiguous lattice sites are formed through potential interactions during irreversible adiabatic expansion of an activated region near the surface surrounding the impact site.

CHEMICAL REACTIONS OF N_2^+ ION BEAMS WITH FIRST-ROW TRANSITION METALS

by

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ABSTRACT

Ion beam studies of chemical reactions between nitrogen and surfaces of the first-row transition metals are reported. X-ray photoelectron spectroscopy (XPS) and thermal desorption mass spectrometry under ultrahigh vacuum conditions are used to examine the products induced by 30-3000 eV N_2^+ beams on the polycrystalline metal foils. The reaction results in the formation of metal nitrides which are similar to the pure metal nitride compounds. The amount of nitrogen reacting with the metal can be correlated to the enthalpy of formation of the metal nitride. Estimates of the thickness of the reacted layer are obtained from LSS projected ion range calculations. The chemical nature of the reaction is supported by identification of the products through energy level shifts and by the agreement with thermodynamic predictions. A mechanism is proposed for the reaction which involves charge exchange neutralization and dissociation of the ion at the surface followed by penetration into the lattice, thermalization, and finally chemical reaction.

* R. A. Welch Predoctoral Fellow

SECONDARY ION MASS SPECTROMETRY OF MOLECULAR SOLIDS: CLUSTER
FORMATION DURING ION BOMBARDMENT OF FROZEN H_2O , C_6H_6 , AND C_6H_{12}

by

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ABSTRACT

The secondary ion mass spectra (SIMS) of H_2O , C_6H_6 , and C_6H_{12} frozen at 77°K are reported. The spectra are generated by subjecting the molecular surface to 0.5 - 3 keV He^+ ions and mass analyzing the positive and negative secondary clusters in a quadrupole mass filter. The most abundant clusters in the H_2O spectrum were of the type $\text{H}(\text{H}_2\text{O})_n^+$, $n=1,2,\dots,51$ although other low intensity clusters were also observed. The benzene and cyclohexane spectra exhibited clusters of the type C_nH_m^+ , $n=1,2,\dots,32$ and $m=1,2,\dots,10$. The intensities, I , of the different types of cluster series observed from H_2O vary as a function of the number of H_2O molecules, n , in the cluster according to $I = ae^{bn}$ where a and b are constants. The kinetic energy distributions of the clusters have a maximum in the region 1.0 - 3.3 eV which, in general, shifts to lower energy and sharpens with increasing cluster size. A general clustering mechanism which is qualitatively consistent with all of the experimental observations is proposed. This mechanism involves thermal activation by the primary ion impact and irreversible adiabatic expansion to relieve the nonequilibrium situation. Bound clusters are formed from collections of secondary particles moving through the selvedge region of the surface. The formation of a tightly bound cluster

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only as the particles are moving through the surface accounts for the molecular rearrangement observed during sputtering.

*R. A. Welch Foundation Predoctoral Fellow

MACROMOLECULAR IONIC CLUSTERS OF WATER DETECTED BY SIMS

by

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ABSTRACT

Ion clusters can be detected with mass up to 919 amu containing as many as 154 atoms, e.g., $\text{H}(\text{H}_2\text{O})_{51}^+$ in the secondary ion mass spectrum (SIMS) of ice. The clusters are of the type $\text{H}(\text{H}_2\text{O})_n^+$, $n = 1, 2, \dots, 51$ and have lifetimes greater than 0.9 msec in the gas phase. These are the largest cluster ions of water that have been produced by sputtering and the largest clusters detected by the method of static SIMS to date. The relative abundance of the clusters with $n = 3, 4$, and 21 are greater than their neighbors, indicating that there is a peculiar stability associated with these clusters.

*R. A. Welch Foundation Predoctoral Fellow

SIMS STUDY OF THE MECHANISM OF CLUSTER FORMATION
DURING ION BOMBARDMENT OF ALKALI HALIDES

by

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ABSTRACT

The secondary ion mass spectra (SIMS) of the salts NaX (X = F, Cl, Br, I) and CsX (X = F, I, ClO₄) are reported. A UHV spectrometer system designed for SIMS studies is described in detail. Large secondary ion clusters of high mass, e.g., Na₁₄F₁₃⁺ (569 amu) and Cs₄I₃⁺ (913 amu), whose minimum lifetimes are of the order of tenths of milliseconds, have been detected. The long series of detected cluster ions of the type M_nX_{n-1}⁺ indicates that there is a high degree of stability associated with these clusters. The intensities, I, of the different series of observed clusters of the type M_nX_{n-m}⁺ (m = -2, -1, 0, 1, 2) vary as a function of cluster mass M according to $I = aM^b$, where b takes values from -1.98 to -9.02 for various series. The kinetic energy distributions of the clusters have a maximum in the region 1-2 eV which, in general, shifts to lower energy and sharpens with increasing cluster size. A clustering mechanism which is qualitatively consistent with all of the experimental observations is proposed. This mechanism involves formation of a bound cluster from a collection of secondary particles moving through the selvedge region of the surface as a result of a single primary ion collision. The formation of a tightly bound cluster after the particles are moving through the selvedge region accounts for the molecular rearrangement observed during sputtering.

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CHEMISORPTION OF CO ON (10 $\bar{1}$ 1) TITANIUM

STUDIED BY XPS, UPS, FDMS, AND AIB

by

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ABSTRACT

Chemisorption of CO on the clean (10 $\bar{1}$ 1) face of a titanium single crystal has been investigated by the techniques of x-ray and UV photoelectron spectroscopy (XPS and UPS), flash desorption mass spectrometry (FDMS), and active ion bombardment (AIB). CO is dissociatively chemisorbed at room temperature to form oxide- and carbide-like species. The (10 $\bar{1}$ 1) face of Ti is very active; the sticking probability for CO is unity below 0.6 L (1 L = 10⁻⁶ Torr sec) and the surface is saturated at 2 L exposure. Approximately 1% of the chemisorbed CO is desorbed upon heating to 300°C by a mechanism which does not follow simple first-order kinetics. The C and O remaining on the surface at 300°C form titanium carbides and oxides which migrate into the bulk of the crystal between 300 and 500°C. AIB with 500 eV CO⁺ produces carbides and oxides that are identical to the species on the surface at 300°C. High kinetic energy AIB results in complete dissociation of the CO⁺ into atoms, thus confirming that chemisorbed CO is dissociated on the (10 $\bar{1}$ 1) face of Ti.

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AIB INDUCED CHEMICAL REACTIONS AT SURFACES DETECTED BY SIMS

by

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ABSTRACT

Secondary ion mass spectrometry (SIMS) has been used to detect the reactions induced by active ion bombardment (AIB) of N_2^+ on surfaces of pyrolytic graphite and a (100) Si crystal. The SIMS spectra exhibit ions of CN^- , HCN^- , $H_n C_2 N^-$ ($n = 2, 3, 4$), HN^- , and SiN^- , indicating that reactions take place with the graphite and silicon as well as adsorbed hydrogen on the surfaces.

PHASE TRANSFORMATION (hcp→bcc) ON A $(10\bar{1}1)$ TITANIUM SURFACE

STUDIED BY He II UPS

by

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ABSTRACT

He II (40.8 eV) UPS spectra of clean $(10\bar{1}1)$ titanium have been measured for sample temperatures up to 960°C and the full-width-at-half-maximum (FWHM) of the d-band has been monitored as a function of temperature. The FWHM of the d-band increased at 800°C and retained a constant value above this temperature. These results indicate that the phase transformation (hcp→bcc) on the Ti surface occurs about 80°C below the bulk critical temperature. The FWHM of the d-band of polycrystalline hcp Ti is 0.6 eV greater than that of single crystal hcp Ti. The density of states [states/(atom eV)] at the Fermi level $n(E_F)$ shows no significant changes between the hcp and bcc structures.

SURFACE ALTERATION OF GRAPHITE, GRAPHITE MONOFLUORIDE AND TEFLON
BY INTERACTION WITH Ar^+ AND Xe^+ BEAMS

by

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ABSTRACT

Ion beam studies of the interaction of Ar^+ and Xe^+ with surfaces of pyrolytic graphite, graphite monofluoride and teflon are reported. The techniques of X-ray and UV photoelectron spectroscopy (XPS and UPS) and thermal desorption mass spectrometry under UHV conditions are used to examine the surfaces of the materials after bombardment with 30-3000 eV rare gas ions. Implanted rare gases from a 500 eV beam in doses of $\sim 1.5 \times 10^{-2} \text{ A s/cm}^2$ could be detected only in graphite and graphite monofluoride, although reduced carbon species were formed in both teflon and graphite monofluoride. The binding energies of the implanted rare gases indicate that they are trapped as neutral atoms within the lattice. Evolution of Xe from graphite is maximum at $\sim 375^\circ\text{C}$. Approximately 2.8% of the Xe^+ and 5.6% of the Ar^+ ions from the beam remain trapped in graphite; the amount trapped in graphite monofluoride is about one order of magnitude less than this.

* R. A. Welch Foundation Predoctoral Fellow

VACUUM ULTRAVIOLET RESONANCE LINE RADIATION SOURCE FROM
RARE GAS ATOMS AND IONS FOR UHV PHOTOELECTRON SPECTROSCOPY

by

G. M. Lancaster*, J. A. Taylor, A. Ignatiev, and J. W. Rabalais

ABSTRACT

A source and differential pumping system for producing high intensity resonance line radiation from rare gas atoms and ions for ultrahigh vacuum (UHV) photoelectron spectroscopy has been developed. Photoelectron count rates from a gold sample, as measured with a double-pass cylindrical mirror analyzer at pass energy 15 eV and 0.10 eV resolution, are $\sim 300,000 \text{ cs}^{-1}$ for the He(I) (21.22 eV) line and $\sim 30000 \text{ cs}^{-1}$ for the He(II) (40.81 eV) line. The source design is based on the principle of the electrostatic charged particle oscillator and is capable of sustaining discharges over the pressure range 1 to $\sim 10^{-6}$ torr. The discharge segment consists of a cylindrical cold cathode surrounding two tungsten rod anodes which are held at high positive potential. Three stages of differential pumping are employed in order that the vacuum in the main spectrometer chamber can be maintained at 2×10^{-10} torr during operation. The calculated helium flow reaching the main chamber under these conditions is $< 10 \text{ l s}^{-1}$. Details of the construction and operating characteristics of the source are presented.

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HIGH MASS SECONDARY ION CLUSTER OF
CAESIUM IODIDE DETECTED BY SIMS

by

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ABSTRACT

The secondary ion mass spectrum (SIMS) of CsI exhibits ion clusters of the type $\text{Cs}_n\text{I}_{n-1}^+$ with mass as high as 913 amu. The most abundant members of the series are Cs^+ and Cs_2I^+ . The energy distributions of these ion clusters were analyzed in a "Bessel box" electrostatic energy prefilter. The Cs^+ and Cs_2^+ distributions are maximum at ~ 2.0 eV and have half widths of 9.0 - 10.2 eV while the Cs_2I^+ and Cs_3I_2^+ distributions are maximum at ~ 1.1 eV and have half widths of 3.2 - 4.2 eV. These contrasting energy distributions for large and small clusters indicates that the mechanisms of cluster formation may be different for different size clusters.

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INTERACTIONS OF N_2^+ AND NO^+ IONS WITH SURFACES OF
GRAPHITE, DIAMOND, TEFLON, AND GRAPHITE MONOFLUORIDE

by

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ABSTRACT

Ion beam studies of the reactions of nitrogen and nitric oxide with surfaces of carbonaceous materials are reported. The techniques of x-ray and UV photoelectron spectroscopy (XPS and UPS) and thermal desorption mass spectrometry under ultrahigh vacuum conditions are used to examine the products induced by 30-500 eV N_2^+ and NO^+ beams on graphite, diamond, Teflon, and graphite monofluoride. The molecular ions undergo charge-exchange neutralization and dissociation at the surface to form hot N and O atoms. Reactions between these hot atoms and the surfaces produce a cyanide- and oxide-type bond with the carbon. In the case of graphite, two different reaction products are observed for reaction with either N or O atoms. It is proposed that one of these is the cyanide- or oxide-type compound and the other is interstitial N or O atoms between the layers of rings or at defect sites in the lattice. A model for this reaction is proposed which includes neutralization and dissociation of the ions followed by surface penetration and deceleration and finally reaction with the atoms of the lattice.

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CHEMICAL REACTIONS OF N_2^+ ION BEAMS WITH
GROUP IV ELEMENTS AND THEIR OXIDES

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ABSTRACT

Ion beam studies of the reactions between nitrogen and surfaces of Group IV elements and their oxides resulting nitride formation are reported. XPS and UPS are used to examine the products induced by 500 eV N_2^+ beams on diamond, graphite and elemental Si, Ge, Sn, Pb and their oxides. Nitrogen adds to the graphite in two positions: at the carbon rings and intersitually between the layers of rings. Reaction with Se, Ge and Sn produces nitrides which are similar to those of the type M_3N_4 . Reaction with oxides forms nitrides with no evidence of nitrate or nitrite formation. The chemical nature of the reaction is supported by identification of the products through energy level shifts and by the agreement with thermodynamic predictions.

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